

Renewable cyclic monomers for high-performance biobased polyesters

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Valorization addendum

The common goal in this PhD research was to develop high performance polymer materials from new biobased building blocks. High performance polymers are a group of polymers which have good mechanical, thermal, and chemical properties, which are retained under various “working” conditions: The performance should be good and stable during *e.g.* mechanical loading, change in temperature or medium. Currently such high performance properties are often gained by (co-)polymerization of rigid building blocks such as cycloaliphatic 1,4-cyclohexanediol and 1,4-cyclohexanedimethanol. These building blocks are typically used as (co-)monomer to increase, amongst others, the thermal stability and melt-strength of polymers. A well known example is the co-polymerization of 1,4-cyclohexanedimethanol in PET which strongly enhance the toughness. The rigid cyclohexane-ring gives rise to these beneficial properties, however currently most of such rigid (co-)monomers used are sourced from petrochemical. Hence, this research is set out for the development of (novel) renewable cycloaliphatic monomers, which can be used as a renewable alternative.

As already described in detail in chapters 1-3 in this thesis, in our hands polyesters based on the potentially renewable building block 1,3-cyclopentanediol could not be used in performance polymers. This is mainly related to the inherent thermal instability of the hydroxyl end-groups limiting the temperature for melt-polycondensation. Also the obtained polyesters with 1,3-cyclopentanediol were not stable, which resulted in degradation upon melt, thus effectively preventing melt-processing. Further use of 1,3-cyclopentanediol as co-monomer proved challenging to synthesize high molecular weight polyesters, and did not result in result in beneficial properties on *e.g.* the glass transition temperature (T_g).

In contrast, the developed cyclic monomers based on the cascade aza-Michael addition-cyclization between itaconic acid and various diamines proved to be highly interesting (Chapter 4, this thesis). The use of cyclic diamines such as *trans*-1,4-cyclohexanediamine (*t*-CH) and *para*-phenylenediamine (*p*-Ph) yielded tri-cyclic bis-pyrrolidone monomers: *t*-CH-BPDA and *p*-Ph-BPDA (Chapter 5, this thesis). Polyesters based on these BPDAs with 1,10-dodecanediol have good thermal properties, likely originating from the rigid tri-cyclic BPDA moieties. Especially the drawn tapes of poly([*t*-CH-BPDA]-C₁₀) and poly([*p*-Ph-BPDA]-C₁₀) show very promising mechanical properties (Chapter 6 this thesis). Indeed, this chapter beautifully shows how the polymer properties are determined by 3 factors: chemistry, molecular weight, and processing. With these 3 parameters right we obtained brittle to ductile transition (molecular weight), brittle to strong crystals (processing), increase in T_g (processing), high melting (chemistry) and water resistant (chemistry) properties for a new class of polyester, which is ~80% biobased. Even though the development of these polymers is still in the very beginning,

we can think of two possible target applications: strong fibers, and heat-shrink polymers tunable for the shrink temperature (e.g. body temperature) with high water stability and biocompatibility.

Poly([*t*-CH-BPDA]-C₁₀)

The good mechanical properties of drawn tapes of poly([*t*-CH-BPDA]-C₁₀) with oriented crystals can be at the basis of further development of these fibers. Current drawing experiments have been performed at room temperature (r.t.), with a separate annealing step at 60 °C. Annealing in the drawn state lead to the formation of the oriented crystals, giving an increase in mechanical properties, whilst remaining ductile. This batch-wise process is undesirable for larger scale processing, hence a logical next step would be to study the crystallization rate during drawing. This can be performed by *in situ* XRD measurements (e.g. at synchrotron facilities at Grenoble or Alba), where the effect of draw rate at various temperatures can be measured on the crystallization. The results of these measurements can then function as a base for the production of fibers from a melt-extrusion spinning line as present within the AMIBM laboratories (Figure 1). During melt-extrusion the molten polymer can be pushed through a spin-plate with small nozzles, from which the polymer can be pulled into small fibers. The fibers pass through an air quench step to produced amorphous fibers, similar to how the polymer films described in Chapter 6 are quenched. Subsequently these quenched amorphous fibers can be drawn by the rotating godets at various temperatures, to obtain the desired orientation and crystallization.

There is a wide range of applications for polymeric fibers, including producing yarns for various textile products. The direct applications for fibers (or tapes) from our developed polyester is still uncertain, as first several key parameters need to be studied. These include the temperature stability, (effect of) moisture absorbance, chemical stability, biocompatibility and biodegradation/biotoxicity. Though we estimate the temperature stability is high (T_m of oriented crystals is around 180 °C), moisture absorbance is minimal, and therefor has a high stability in aqueous environment (stable against hydrolysis at r.t.). In terms of biocompatibility preliminary cytotoxicity tests have been performed on amorphous isotropic films of both developed polyesters in collaboration with the MERLN institute (Rebeca Rivero, dr. Matt Baker). The polymer films were tested with a Presto Blue cell viability assay via cell-contact measurements on L929 cells. L929 cells were seeded in 96-well plates, and after one day a piece of the polymer was placed in contact with the cells and incubated for 24 and 48 h at 37 °C. After those times the polymer piece was removed, and the Presto Blue solution was added to the wells and further incubated for 1 h at 37 °C. The fluorescent intensity between the control (polystyrene), poly([*p*-

Ph-BPDA]-C₁₀) (polymer 1) and poly([*t*-CH-BPDA]-C₁₀) (polymer 2) are not significant after 48 h, indicating absence of toxicity (Figure 2).

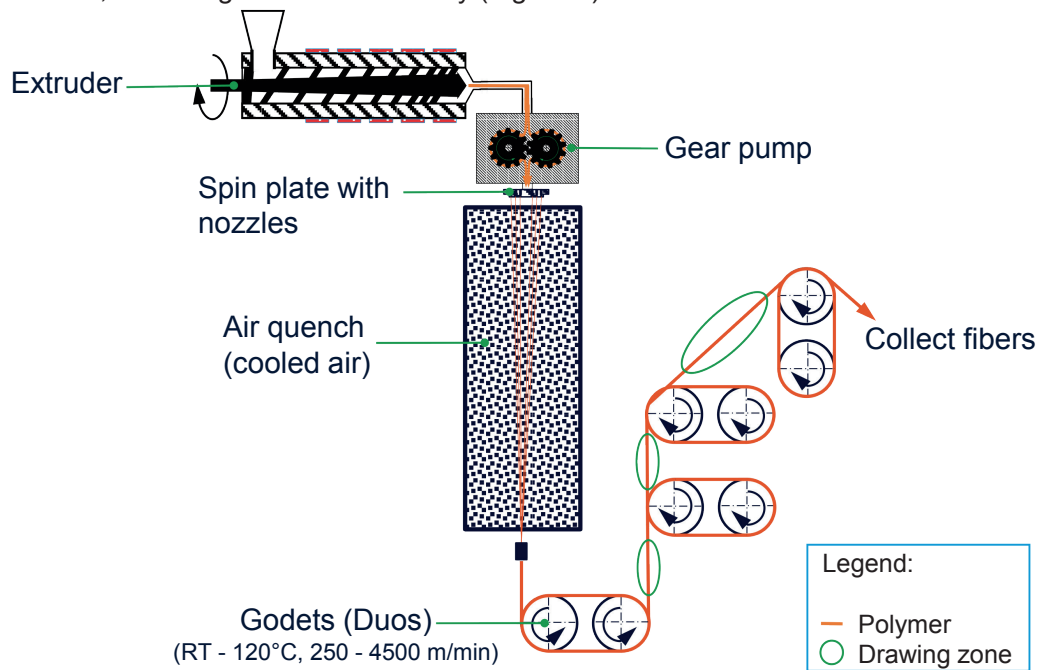


Figure1. Schematic overview of melt-extrusion line to produce oriented polymeric fibers as present in the laboratories of AMIBM (image courtesy of Stefan Hermanns). Melt-extruded polymer is pumped through a spin plate with nozzles, from which polymer fibers are drawn. The fibers are first quenched by cooled air, and subsequent drawing steps are realized on multiple rotating godets, which can rotate at different speeds and temperatures to obtain the preferred draw ratio and crystallization.

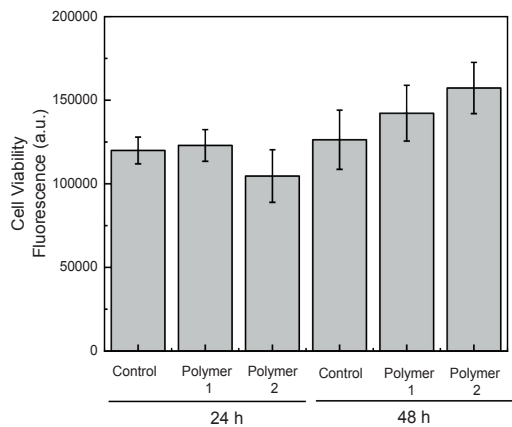


Figure 2. Presto Blue cell viability assay via cell-contact measurements on L929 cells for our developed polyesters poly([*p*-Ph-BPDA]-C₁₀) (polymer 1) and poly([*t*-CH-BPDA]-C₁₀) (polymer 2), controlled against polystyrene. After 48 h there is no significant difference between our polymers and the control, indicating absence of toxicity for cell-contact.

Though these (bio)toxicity experiments are very preliminary, it is at least good to know that cells do not immediately die upon contact with our developed polyesters. A next step would be to perform controlled biodegradation (e.g. in enzymatic solution) or hydrolysis (e.g. in hot water), and study the biotoxicity of the obtained products. If biotoxicity indeed proves to be low it is also important to study whether cells or not can grow on the polyester surface. If so this can open up interesting possibilities for *in vivo* applications for our developed polyesters.

Poly([*p*-Ph-BPDA]-C₁₀)

In contrast to the poly([*t*-CH-BPDA]-C₁₀) drawn tapes, the drawn tapes of poly([*p*-Ph-BPDA]-C₁₀) proved much harder to crystallize in the drawn state. Rather, we observed the rapid shape memory behavior as soon as the oriented tapes are heated to above their T_g . Such shape memory behavior is typical for polymers which are kinetically trapped in the stretched state, and applications are commonly found in heat shrink foils. Also, as discussed in Chapter 6, the T_g changes as a function of the drawing ratio, and as described in Chapter 5, the T_g also changes depending on the diol spacer length. It would be interesting if the temperature trigger for the shape memory behavior around body temperature (38–40 °C). This can be achieved by increasing the diol spacer length to e.g. C₁₂ diol, after which the draw ratio will determine the final trigger temperature. If the biocompatibility of this polymer is indeed good, there are some interesting *in vivo* applications for heat shrink materials which shrink at body temperature. For example, there are applications where an expanded tubular polymer is placed over a (repaired) blood vessel, which after a mild temperature treatment contracts and forms a fixed bandage over the blood vessel. One important thing to investigate is the need for mechanical performance of these heat shrink foils during application. As we have seen in Chapter 6, the drawn state of poly([*t*-CH-BPDA]-C₁₀) is a tough material, but the amorphous isotropic state (as it will be after heat shrinkage) is soft and readily deforms.

Scaling up

Scaling up and marketability is highly dependent on pricing and availability of the used monomers. The main bottle-neck is *trans*-1,4-cyclohexanediamine (*t*-CH), which is not produced as commodity chemical, and is highly expensive: currently ranging around €1000/kilo at commercial suppliers. However, its precursor, and also one of our monomers, is *para*-phenylenediamine (*p*-Ph) which is produced cheaply on industrial scale. At this moment *p*-Ph is not available from biomass, and thereby limiting the biobased content in our developed polyesters to about 80% (atom-based). An interesting research project to set up would be to develop a biobased route towards *p*-Ph. This could be initiated with a research collaboration with the start-up BioBTX, which could produce the required raw material from biomass. In turn, this can be used as a drop-in in existing chemical plants to produce *p*-Ph. Further hydrogenation towards *t*-CH and subsequent separation of the isomers is currently performed batchwise in low quantities. However,

with a potential market pull from our developed polymers it can be worthwhile to develop a route and perform a cost-optimization to estimate the costs of the final polymer if these routes are developed.

End of life?

A very important factor in the ecological footprint of polymers is not only the sourcing, but also the end-of-life options. Currently, a lot of money is invested to enhance the waste-management and recycling technologies to obtain clean waste-streams of plastic ready to be reprocessed. The recycling efficiency is determined by two main parameters: the amount of material that can be recycled (% of total volume), and purity of the recycled fraction. Unfortunately, at the current technology level, introducing new (biobased) plastics to the market will inherently lead to an even more complex waste stream of plastic materials to sort, potentially negatively influencing the recycling efficiency. However, it is not very relevant to highlight this too much at this stage, as the total market volume at this moment for biobased plastics is hovering around 1%. Furthermore, recyclers use near-infrared (NIR) technologies to identify and separate the different plastics in the recycling stream. The newly developed biobased plastics have a unique NIR signal, and will easily be removed from the waste streams, avoiding pollution of the waste streams of e.g. PET, PE, PP. More importantly, the majority of the plastics produced today do not follow the “design to recycle” principle, which is visible in the large variety of additives and multilayer filaments, effectively reducing the recycling efficiency by making “inferior mixed granulates”. So if the potential increase of complexity of the plastic waste streams would be an argument against biobased plastics on the market, then the same holds true for the production of mixed-plastic (packaging) on the market which are not designed to recycle.

Alternatively, we can learn from the current end-of-life options for the biobased polymer PLA. Even though PLA can excellently be recycled, the current production and market volume of PLA is so low that installing a separate waste-stream at plastic recyclers is not worth the investment. Rather, many PLA products are sold and labelled as industrial compostable, which means that consumers can dispose of their PLA products in the green bin at home. Although from an environmental point of view recycling is of course much better than composting, at the current production scales industrial composting is a viable alternative. The use, and end-of-life, of PLA can function as an excellent example for the development of other high-performance biobased polymers. With this in mind it would be good, if larger scale production of our developed polyesters will happen, to study whether industrial composting is a viable end-of-life solution. Obviously when production volumes further increase direct recycling routes should be developed for all new (biobased) polymers, perhaps via new deposit-schemes as currently exists for some PET bottles, or by installing extra NIR-separating lines at the plastic recyclers.